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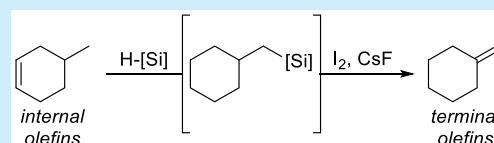
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Contra-thermodynamic Olefin Isomerization by Chain-Walking Hydrofunctionalization and Formal Retro-hydrofunctionalization

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ABSTRACT: We report a contra-thermodynamic isomerization of internal olefins to terminal olefins driven by redox reactions and formation of Si–F bonds. This process involves chain-walking hydrosilylation of internal olefins and subsequent formal retro-hydrosilylation. The process rests upon the high activities of platinum hydrosilylation catalysts for isomerization of metal alkyl intermediates and a new, metal-free process for the conversion of alkylsilanes to alkenes. By this approach, 1,2-disubstituted and trisubstituted olefins are converted to terminal olefins.



A fundamental principle of the chemistry of alkenes is that internal olefins are more stable than terminal olefins. This greater stability originates from a hyperconjugative interaction between the alkyl substituents and the π^* orbital of an olefin. Because the isomerization of terminal olefins to internal olefins is exergonic, many such isomerizations have been reported (Scheme 1). Classical methods for the isomerization of olefins involve proton transfers catalyzed by acid or base. Transition-metal-catalyzed isomerizations of alkenes occur by one of several pathways shown in Scheme 1,¹ but all such catalytic isomer-

izations involve the conversion of terminal olefins to internal olefins or the conversion of one internal olefin to another internal olefin because terminal olefins are less stable than internal olefins.

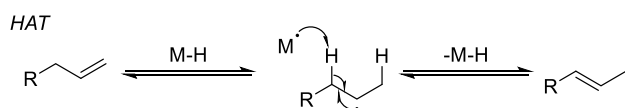
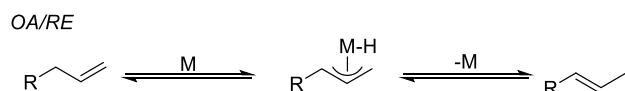
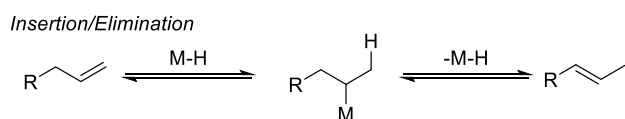
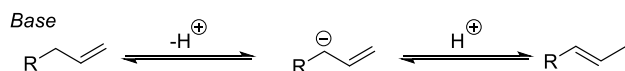
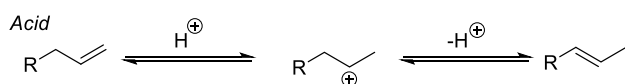
Inspired by biological processes in which downhill hydrolyses and redox processes are coupled to thermodynamically uphill steps, we sought to develop one or more exergonic chemical processes that could be coupled to an endergonic isomerization of internal olefins to terminal olefins. The term contra-thermodynamic describes reactions that couple an increase in free energy of one synthetically valuable process to additional exergonic processes. Several multistep approaches to contra-thermodynamic olefin isomerization have been reported;² however, strategies to form the terminal alkene with high selectivity have been limited to translocation of a double bond by only one carbon unit.³ No examples of reactions that lead to the selective migration of a double bond beyond a single carbon unit have been reported previously.

Such a method for the selective, contra-thermodynamic translocation of a double bond over multiple carbon units would enable chemists to conduct subsequent reactions at sites that are remote from the starting alkene. For example, the terminal olefins formed by such an isomerization could undergo a variety of difunctionalizations or hydrofunctionalizations that cannot occur in concert with chain walking of metal–alkyl intermediates. Long-range isomerizations also could be used to modify the structures of natural products, such as terpenes, containing alkenes. Finally, on a different scale, long-range, contra-thermodynamic isomerizations could enable the valorization of mixtures of internal olefins to isomerically pure linear α -olefins.

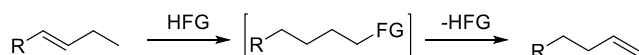
To develop a long-range, contra-thermodynamic olefin isomerization, we envisioned that chain-walking hydrofunctionalization of an internal alkene could be conducted in concert

Scheme 1. Thermodynamic vs Contra-thermodynamic Olefin Isomerizations

Many Reports: Terminal Olefins to Internal Olefins



This Work: Internal Olefins to Terminal Olefins

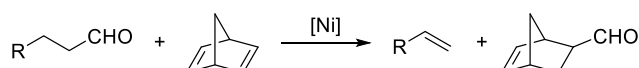


with retro-hydrofunctionalization (Scheme 1: *This Work*). We report the formation of terminal alkenes from internal alkenes by combining platinum-catalyzed hydrosilylation with a new method for the conversion of alkylsilanes to terminal alkenes. This process enables the translocation of the carbon–carbon double bond through multiple secondary sites, as well as through a combination of secondary and tertiary sites to form the terminal alkene.

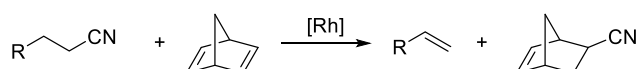
A variety of chain-walking hydrofunctionalizations,⁴ including hydrosilylations,⁵ hydroborations,⁶ hydrocyanations,⁷ hydroformylations,⁸ and alkoxy-carbonylations,⁹ are known, and several retro-hydrofunctionalizations have been developed. However, none of these retro-hydrofunctionalizations have been combined with hydrofunctionalizations to enable the contrathermodynamic isomerization of alkenes. Retro-hydrocyanation, which was developed by Morandi, proceeds by the net transfer of hydrogen cyanide to a strained olefin (Scheme 2).¹⁰ A similar retro-hydroformylation developed by Dong

Scheme 2. Retro-hydrofunctionalizations

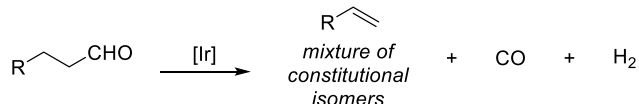
Retro-Hydroformylation (Dong)



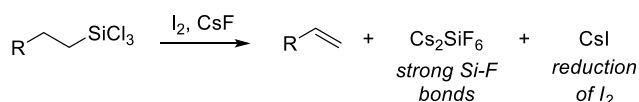
Retro-Hydrocyanation (Morandi)



Retro-Hydroformylation (Nozaki)



Retro-Hydrosilylation (This Work)



involves the net transfer of formaldehyde to a strained olefin, and a retro-hydroformylation reported by Nozaki involves the extrusion of synthesis gas from the system.¹¹ While retro-hydrocyanation and retro-hydroformylation have been developed, the *n*/*iso* ratios of chain-walking hydrocyanations and chain-walking hydroformylations are lower than those of other chain-walking hydrofunctionalizations, and the current catalysts for these transformations rarely undergo isomerization through tertiary centers (Keuleman's rule).

In contrast to chain-walking hydroformylations and hydrocyanations, platinum-catalyzed hydrosilylations proceed with exceptionally high *n*/*iso* ratios because the catalyst undergoes fast isomerization of internal metal alkyls to terminal metal alkyls and selective reductive elimination of the terminal metal alkyl intermediate with the silyl group. In addition, chain-walking hydrosilylations of internal olefins with trichlorosilane proceed without solvent and with low loadings of Speier's catalyst (H_2PtCl_6), making this class of hydrofunctionalization conducive to the development of a one-pot isomerization. Finally, platinum catalysts for hydrosilylation "walk" through tertiary

centers, a prerequisite for movement of a double bond through branched portions of a molecule. However, retro-hydrosilylation is not a known reaction.¹²

Retro-hydrosilylation is challenging to develop because the microscopic reverse of hydrosilylation involves the oxidative addition of a C–Si bond, which is a rare reaction. Therefore, we designed a new approach to the conversion of alkylsilanes to olefins. By this process, the typically nucleophilic silyl group would be oxidized to a nucleofuge, which would undergo base-promoted conversion to a terminal olefin. Specifically, alkylsilanes would be oxidized to alkyl halides through pentafluorosilicate intermediates,¹³ and the resulting alkyl halides would undergo classical eliminations *in situ*. In contrast to the retro-hydrofunctionalizations driven by the release of ring strain or by the extrusion of gases, this approach would couple the endergonic retro-hydrosilylation to the exergonic reduction of iodine and formation of strong Si–F bonds. The approach would constitute a formal retro-hydrosilylation because it does not proceed by the microscopic reverse of hydrosilylation.

To test this design, we conducted the reaction of branched alkylsilane **2a** with an oxidant and a fluoride source (Table 1).

Table 1. Formal Retro-hydrosilylation of β -Branched Alkylsilanes

entry	change from above conditions	yield of 3a ^a
1	none	82%
2	6 equiv of CsF	0% ^b
3	KF instead of CsF	31%
4	2 equiv of I ₂	73%
5	ACN instead of DMF	68%
6	<i>i</i> PrOH instead of DMF	60%
7	toluene instead of DMF	0% ^b
8	NIS instead of I ₂	9%
9	NBS instead of I ₂	0%
10	50 °C	48%

^aYields were determined by ¹H NMR spectroscopy with trichloroethylene as an internal standard. ^bMajor product observed was alkyl iodide intermediate.

We imagined that treating this silane with cesium fluoride and iodine would trigger a domino sequence involving the formation of a pentafluorosilicate, iodination of the C–Si bond, and elimination from the resulting alkyl iodide. Indeed, silane **2a** reacted with cesium fluoride and iodine in DMF for 20 h at 100 °C to form 4-*tert*-butylmethylenecyclohexane (olefin **3a**) in 82% yield (entry 1); in this process, the cesium fluoride functions as both a reagent for activation of the silane and a base for elimination of the halide. In the presence of 6 equiv of CsF, olefin **3a** formed in only trace amounts (entry 2). In this case, the corresponding alkyl iodide was the major product formed, indicating that the formal retro-hydrosilylation process can be stopped prior to elimination. Reactions with KF in place of CsF (entry 3), larger numbers of equivalents of I₂ than 1.1 (entry 4), or solvents other than DMF (entries 5–7) gave olefin **3a** in lower yields than reactions conducted with the standard conditions in entry 1. Although NIS and NBS are known to halogenate alkyl pentafluorosilicates, these compounds were not suitable oxidants for this transformation (entries 8–9). A lower

yield was observed when the formal retro-hydrosilylation was conducted at 50 °C instead of 100 °C (entry 10).

Upon subjecting the linear alkylsilane **2b** to the conditions developed for the formal retro-hydrosilylation of branched silane **2a**, a significant quantity of *n*-octadecyl fluoride (**4b**) formed, along with terminal olefin **3b** (Table 2, entry 1). This

Table 2. Formal Retro-hydrosilylation of Linear Alkylsilanes^a

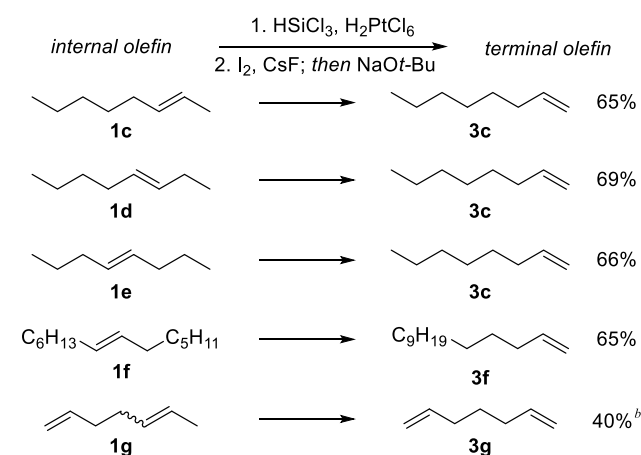
${}^n\text{C}_{18}\text{H}_{37}\text{SiCl}_3 \xrightarrow[\text{NaOt-Bu}]{\text{I}_2, \text{CsF}} \text{C}_{15}\text{H}_{31} + {}^n\text{C}_{18}\text{H}_{37}\text{F} + {}^n\text{C}_{18}\text{H}_{37}\text{I}$				
entry	CsF (equiv)	yield 3b ^b	yield 4b ^b	yield 5b ^b
1 ^c	10	54%	23%	0%
2 ^c	6	0%	0%	62%
3	6	65%	0%	0%
4 ^d	6	0%	0%	0%
5 ^e	6	33%	0%	10%

^aConditions: Silane (0.1 mmol), Iodine (1.1 equiv), CsF, DMF, 100 °C, 20 h; NaOt-Bu (5 equiv), rt, 20 h. ^bYields were determined by ¹H NMR spectroscopy with trichloroethylene as an internal standard. ^cNo second step conducted. ^dBoth steps conducted simultaneously. ^eUnder air, no protection from light.

result indicates that that alkyl iodide intermediates lacking β -branching undergo competitive $\text{S}_{\text{N}}2$ and E2 processes with cesium fluoride. We hypothesized that arresting the formal retro-hydrosilylation of silane **2b** at alkyl iodide **5b** by conducting the iodination process with exactly 6 equiv of CsF would enable the elimination to be conducted with a base known to favor E2 elimination over $\text{S}_{\text{N}}2$ substitution. Indeed, the reaction of silane **2b** with 6 equiv of CsF formed *n*-octadecyl iodide in 62% yield, along with trace olefin and no alkyl fluoride (entry 2). Treatment of this crude reaction mixture with a hindered alkoxide base (NaOtBu) at room temperature led to a classical elimination reaction and provided olefin **3b** in 65% overall yield (entry 3).

Having developed conditions for the formal retro-hydrosilylation of both linear and β -branched alkylsilanes, we hypothesized that this reaction could be conducted on crude silanes prepared by chain-walking hydrosilylation. In this case, a one-pot, contra-thermodynamic olefin isomerization would result. Indeed, treatment of a variety of internal olefins with HSiCl_3 in the presence of Speier's catalyst and subsequent subjection of the crude alkylsilane to the conditions that induce formal retro-hydrosilylation gave terminal olefins in good yields with excellent *n/iso* selectivities (Scheme 3). No internal olefins were observed by ¹H NMR spectroscopy in any of the crude samples; that is, the *n/iso* ratios of the products were all greater than 99:1. Internal olefins **1c**, **1d**, and **1e** underwent isomerization to 1-octene (olefin **3c**) in moderate to good yields, indicating that both short-range and long-range isomerizations occur. In fact, 7-tetradecene (olefin **1f**) underwent isomerization over six positions to form 1-tetradecene (olefin **3f**) in good yield. Diene **1g**, which contains a terminal olefin and an internal olefin, underwent isomerization to α,ω -diene **3g**, the sole diene formed in the reaction. In this case, the quantity of each reagent was twice that of reactions of substrates lacking pendant alkenes because both olefins underwent hydrosilylation and formal retro-hydrosilylation. This example demonstrates that terminal olefins are tolerated passively because hydrosilylation–retro-hydrosilylation sequences on terminal alkenes are degenerate.

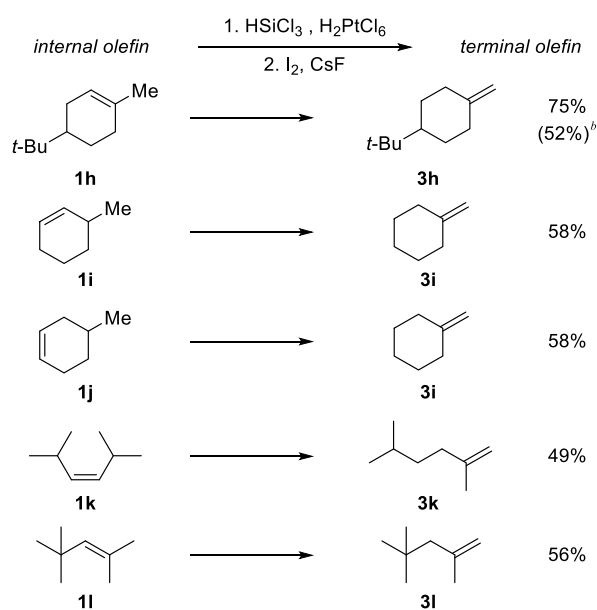
Scheme 3. Contra-thermodynamic Isomerizations of Internal Olefins to α -Olefins^a



^aStep 1: Internal olefin (1 mmol), HSiCl_3 (2 equiv), H_2PtCl_6 (0.2 mol % in 2 μL of isopropanol), 100 °C, 20 h, neat reaction, sealed vessel. Step 2: I_2 (1.1 equiv), CsF (6 equiv), DMF (0.25 M), 100 °C, 20 h; then NaOt-Bu, rt, 20 h. Yields were determined by ¹H NMR spectroscopy with trichloroethylene as internal standard. ^b10 equiv of CsF, 2.2 equiv of I_2 , and 10 equiv of NaOt-Bu.

In addition to isomerizations through linear alkyl chains, isomerizations through branched chains that entail the formation of tertiary metal alkyl intermediates occurred (Scheme 4). For example, cyclic, trisubstituted olefin **1h** underwent isomerization to the 1,1-disubstituted olefin **3h** in good yield. Long-range isomerizations of endocyclic olefins **1i**

Scheme 4. Contra-thermodynamic Isomerization of Internal Olefins through Branched Alkyl Chains to 1,1-Disubstituted Olefins^a

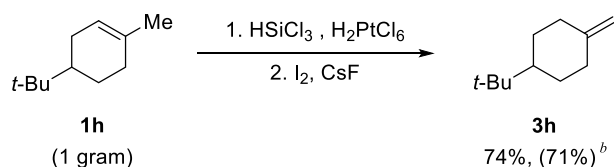


^aStep 1: Internal olefin (1 mmol), HSiCl_3 (2 equiv), H_2PtCl_6 (0.2 mol % in 2 μL of isopropanol), 100 °C, 20 h, neat reaction, sealed vessel. Step 2: I_2 (1.1 equiv), CsF (10 equiv), DMF (0.40 M), 100 °C, 20 h. Yields were determined by ¹H NMR spectroscopy with trichloroethylene as internal standard. ^bIsolated yield indicated in parentheses.

and **1j** to terminal olefin **3i** through tertiary centers also occurred in good yields. Acyclic olefins also underwent isomerization through branched alkyl chains. For example, the long-range isomerization of acyclic 1,2-disubstituted olefin **1k** to 1,1-disubstituted olefin **3k** proceeded in good yield. In addition, the isomerization tolerates steric hindrance at the starting alkene. Conversion of the hindered, trisubstituted olefin **1l**, which bears a *tert*-butyl substituent α to the double bond, to olefin **3l** occurred in good yield.

Finally, this type of contra-thermodynamic isomerization can be conducted on large scales. The isomerization of olefin **1h** to olefin **3h** occurred in 71% isolated yield on a gram scale (Scheme 5).

Scheme 5. Contra-thermodynamic Isomerization on a Gram Scale^a



^aStep 1: Internal olefin (6.2 mmol), HSiCl₃ (2 equiv), H₂PtCl₆ (0.2 mol % in 13 μ L of isopropanol), 100 °C, 20 h, neat reaction, sealed vessel. Step 2: I₂ (1.1 equiv), CsF (10 equiv), DMF (0.40 M), 100 °C, 20 h. Yields were determined by ¹H NMR spectroscopy with trichloroethylene as internal standard. ^bIsolated yield indicated in parentheses.

In conclusion, we have developed a strategy for contra-thermodynamic olefin isomerization that combines chain-walking hydrosilylation with a formal retro-hydrosilylation. While other hydrofunctionalizations could be envisioned to be applicable to this process for the isomerization of alkenes, platinum-catalyzed hydrosilylation was chosen because of its high *n/iso* ratios, compatibility with trisubstituted olefins, low catalyst loadings, and solvent-free conditions. In contrast to previous retro-hydrofunctionalizations, the present retro-hydrosilylation is driven by redox processes and by the formation of strong Si–F bonds. Development of additional isomerizations that proceed through chain-walking hydrofunctionalization and retro-hydrofunctionalization is ongoing. Particular attention is being given to hydrofunctionalizations that are suitable for industrial processes and to those with expanded functional group tolerance.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02695.

Synthetic procedures and analytical data from ¹H NMR and ¹³C NMR spectroscopy (PDF)

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Notes

The authors declare no competing financial interest.

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